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OVERLAP INTEGRALS AND MOLECULAR ENERGIES¹

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I. INTRODUCTION

In their 1931 papers on the quantum theory of valence, Slater and Pauling discussed the conditions governing the strengths of electron-pair bonds according to the Heitler-London theory. They pointed out that the strength of the bond formed between two atoms by an electron on each should tend to be larger the more the regions of space occupied by the two electrons overlap. These regions of space are defined by the one-electron wave functions, or orbitals, occupied by the electrons. The criterion for maximum strength is then that of maximum overlapping of these orbitals.

The best way to gauge the total amount of overlap of two orbitals as an index of bond strength is probably to write down a mathematical expression for each, to form the product of these, and then to take the integral of this product over all space (overlap integral).² (Of course, only the region of space between and close to the two atoms will contribute appreciably.) That is, if χ_a represents the expression for the orbital on one atom, and χ_b for that on the other, the overlap integral, which is commonly symbolized by S , is given by

$$S = \int \chi_a \chi_b \, dv. \quad (1)$$

all space

It may be helpful before proceeding further to try to see a little more clearly why and how it is that just the quantity S enters into the determination of the bond energy. For this purpose, a

consideration of the simple case of the one-electron bond in H_2^+ is convenient, using the MO (molecular orbital) theory of valence. This theory approaches the problem of valence somewhat differently than the more familiar VB (valence-bond, or Heitler-London-Slater-Pauling) theory, but gives similar (though not identical) results as regards the dependence of bond strengths on overlap integrals. The MO theory has the advantage of being applicable to one-electron and three-electron bonds as well as to electron-pair bonds, and of being able to deal more simply than the VB theory with heteropolar bonds, conjugated and aromatic molecules, and so on; in the MO theory, no special concept of resonance among two or more bond structures is needed in these situations.

In H_2^+ , the one electron occupies a bonding molecular orbital, say ϕ , which may be approximately constructed by forming a symmetrical linear combination of ordinary normalized $1s$ atomic orbitals, say $1s_a$ and $1s_b$, of the two atoms a and b . That is,

$$\phi \approx c(1s_a + 1s_b),$$

(2)

$$\text{where } c = 1/(2 + 2S)^{\frac{1}{2}}$$

is a normalizing factor; S here is the overlap integral in which χ_a and χ_b of Eq. (1) are $1s_a$ and $1s_b$ respectively. The factor c is so chosen that $\phi^2 dv$ shall represent the probability of finding the electron in any given small volume dv of space, ϕ of course being a function of position in space, determined by the forms of the simple familiar mathematical expressions for $1s_a$ and $1s_b$. Hence,

$$\int \phi^2 dv = 1;$$

that is, the probability is 1 of finding the electron somewhere. The function ϕ^2 is then a probability density function; when multiplied by the charge $-e$ of an electron, it becomes a charge density function for

the electron. Using (2), one sees that

$$\rho^2 \approx \frac{1}{2}(1s_a^2 + 1s_b^2)/(1 + S) + (1s_a 1s_b)/(1 + S). \quad (3)$$

This divides the total probability or charge density function into three parts, the total magnitude of each of which can be obtained by integrating, as follows:

$$\begin{aligned} \int \rho^2 dv &\approx [1/(2 + 2S)] \int 1s_a^2 dv + [1/(2 + 2S)] \int 1s_b^2 dv + [1/(1 + S)] \int 1s_a 1s_b dv \\ &= (\frac{1}{2})/(1 + S) + \frac{1}{2}/(1 + S) + S/(1 + S), \end{aligned}$$

since $\int 1s_a^2 dv = \int 1s_b^2 dv = 1$, and $\int 1s_a 1s_b dv = S$. It is seen that on the average the fraction $S/(1 + S)$ of the electronic charge is in the overlap region, the remaining fraction $1/(1 + S)$ being centered one half around each of the two nuclei a and b. Or, in other words, the electron spends the fraction $S/(1 + S)$ of its time in the overlap region, and $\frac{1}{2}/(1 + S)$ of its time in a $1s$ orbit on a, and the same on b.

For the case of an electron spending a full half of its time in a $1s$ orbit on nucleus a in the field of nucleus b, and the other half in a $1s$ orbit on b in the field of a, the energy would be the same as if it spent all its time in a $1s$ orbit on one nucleus but in the Coulomb field of the other; in other words, it would be simply the energy of an H atom in the field of an H^+ ion. This energy would differ only moderately from that of an H atom alone in the absence of an H^+ ion. But quantum mechanics says that actually in H_2^+ the fraction $S/(1 + S)$ of the total electron density has been shifted away from both a and b into the overlap region between them; and shows, furthermore, that it is precisely this partial shift of electronic charge into the increased field in the overlap region which is primarily responsible for the stability of H_2^+ . Hence, it is to be expected that the bond energy of H_2^+ should be approximately proportional to $S/(1 + S)$.

Since according to MO theory the same sort of considerations hold for covalent bonding in general as for H_2^+ , it is plausible to suppose that bond energies (more accurately, energies of atomization) may in general be represented by expressions of the form

$$D = \sum_i A_i I_i S_i / (1 + S_i) , \quad (4)$$

the sum \sum_i being taken over all the bonding electrons.

In Eq. (4), each $A_i I_i$ is meant to be a proportionality constant. The reason for writing these in the form $A_i I_i$, rather than just A_i , will be explained in a moment. Since the theory behind Eq. (4) is only rough, it makes sense to treat $A_i I_i$ as an empirical quantity, rather than to try to determine it theoretically. By so doing, one can expect to compensate to a considerable extent for the approximateness of the theory.

However, it is desirable first to take note that on the basis of very simple and general theoretical considerations one expects, for a given value of S_i , larger bond energies for combinations of atoms whose electrons are strongly held (e.g., H atoms) than for those whose electrons are loosely held (e.g., Li atoms). This is because in the former case, with smaller atomic orbitals, the electrons are concentrated in stronger fields of force, closer to the nuclei, so that larger energy effects are involved. Since the energy of bonding may be considered as a modification or perturbation of the original energy of the valence electrons, it is to be expected that it should be more or less proportional to the latter. Now the ionization energy I of a valence electron in an atom is a good measure of its energy in the atom ("binding energy"). It is therefore plausible to write the proportionality factor preceding each $S_i/(1 + S_i)$ in Eq. (4) in the form $A_i I_i$, with I_i to be obtained from spectroscopic or electron impact data on atoms. This

leaves \underline{A} to be determined as an empirical quantity which, it may reasonably be hoped, can be treated as a constant, at least for orbitals of any one type. In an as yet somewhat preliminary study,⁴ this hope has been realized to an encouraging degree with the use of just two values of \underline{A} , one for σ bonds and one for π bonds. [Actually, the procedure used was rather more complicated than that just outlined, but the basic idea and plan was the same: see further discussion below.]

II. DEGREES OF OVERLAP FOR VARIOUS TYPES OF VALENCE ORBITALS

The way in which the overlap integral \underline{S} for a given pair of orbitals varies with the nature of these orbitals, and with the distance between the atoms with which they are associated, can be seen qualitatively by a study of Fig. 1. (Quantitative results are graphed in Fig. 2.) Fig. 1 depicts, rather schematically, the three pure types of valence orbitals ($2s$, $2p\sigma$, and $2p\pi$), and one representative hybrid type ($2t_e$, the tetrahedral hybrid of $2s$ and $2p\sigma$), for the case of two like first-row atoms, say two carbon atoms. For each type of orbital, the figure shows the pair of atoms (\underline{a} and \underline{b}), in every case at the same distance \underline{R} apart, with an orbital of the given type shown attached to both \underline{a} and \underline{b} . Each orbital consists of a region where it is positive (+ signs) and one where it is negative (- signs). (The meaning would not be changed if all signs in the figure were reversed, simultaneously; it is only the relative signs which matter.) The heavy circles or curves outlining the orbitals in the figure inclose the major parts of the regions where the orbitals are of any considerable magnitude. Straight lines like porcupine quills have, however, been drawn extending radially out beyond these bounding curves in order to suggest that the orbitals actually fade away gradually toward zero. The various orbitals have the forms (for either \underline{a} or \underline{b})

$$\left. \begin{aligned}
 \chi_{2s} &= F_{2s}(r) \\
 \chi_{2p} &= F_{2p}(r)\sqrt{3}\cos \theta \\
 \chi_{2p\pi} &= F_{2p}(r)\sqrt{3}\cos \theta' \\
 \chi_{\text{hybrid}} &= \alpha\chi_{2s} + (1 - \alpha^2)^{\frac{1}{2}}\chi_{2p\sigma}
 \end{aligned} \right\} \quad (5)$$

with $\alpha = \frac{1}{2}$ for the tetrahedral hybrid shown; θ_a (or θ_b) is the angle between any radius vector \underline{r}_a (or \underline{r}_b) and the line drawn from the center of a toward that of b (or from that of b toward that of a); θ'_a is a similar angle between \underline{r}_a and any line drawn from the center of a perpendicular to the line a—b. For present purposes, every orbital should be normalized so that $\int \chi^2 dv = 1$, and it will be assumed that F_{2s} or F_{2p} in Eqs. (5) contains a factor which has been adjusted so that this is true.

Referring now to Fig. 1, let it be imagined that R is progressively decreased, in each sketch. It is seen that appreciable overlapping of corresponding a and b orbitals occurs soonest for χ_{2te} , next for $\chi_{2p\sigma}$; then, at considerably smaller R, for χ_{2s} , and finally for $\chi_{2p\pi}$. It is also seen that if R were finally decreased to zero, χ_{2sa} and χ_{2sb} would coincide identically, likewise $\chi_{2p\pi_a}$ and $\chi_{2p\pi_b}$, while $\chi_{2p\sigma_a}$ and $\chi_{2p\sigma_b}$ would also coincide but with reversed sign. From the foregoing discussion, it is now possible to make a rather good estimate of the behavior of the overlap integral $\underline{S} = \int \chi_a \chi_b dv$ as a function of R in each case. At large R, S is zero. For $\chi_{2p\sigma}$ it begins to rise at fairly large R, but before long reaches a maximum, falls at smaller R, becomes negative, and goes to -1 at R = 0. For both χ_{2s} and $\chi_{2p\pi}$, it begins to rise strongly only at rather small R, but keeps on rising steadily to the value +1 at R = 0. For χ_{2te} , overlap begins at even larger R than for $\chi_{2p\sigma}$; like the latter also, S rises to a maximum and then decreases;

but the maximum is very much higher for χ_{2te} , and at smaller R .

These results obtained from Fig. 1 by inspection can be made more precise if mathematical expressions for $F_{2s}(r)$ and $F_{2p}(r)$ are introduced into Eq. (5). S is actually evaluated by integration in each case for any value of R , and the results are then plotted as a function of R . Graphs of this kind are shown in Fig. 2 for all the orbital types of Fig. 1, and for the additional hybrid types χ_{2tr} and χ_{2d1} ($\alpha = (1/3)^{1/2}$ and $(1/2)^{1/2}$ respectively in Eqs. (5)). It will be seen that the behavior of S in each case agrees with what had already been concluded using Fig. 1.

The computations on which Fig. 2 was based were made using somewhat roughly approximate expressions, of the well-known Slater type, for the various orbitals.⁵ These involve putting

$$F_{2s} = F_{2p} = C e^{-Zr/2a_0} \quad (6)$$

in Eqs. (5), where C is a constant depending on Z . Z is an effective nuclear charge smaller than the actual nuclear charge but increasing with the latter, and a_0 is the radius of the $1s$ Bohr orbit for the hydrogen atom (0.529\AA). Extensive numerical tables of Slater-AO overlap integrals are now available for a wide variety of pairs of orbitals and a wide range of R values.⁵

While Slater orbitals are convenient for the calculation of S values because of their relative simplicity, orbitals of the much more accurate SCF (self-consistent-field) type should be used wherever possible. Following is a brief extract from more extensive tables⁶ to illustrate how the SCF differ from the Slater S values for the case of the overlap of two carbon orbitals.

TABLE I

COMPARISON OF SLATER- AND SCF-ORBITAL OVERLAP INTEGRALS
FOR CARBON-CARBON BONDS

R_{CC}	S_{2s}	$S_{2p\sigma}$		$S_{2p\pi}$		$S_{2p\pi}$	
	Slater and SCF	Slater	SCF	Slater	SCF	Slater	SCF
1.20Å	0.51	0.29	0.14	0.75	0.68	0.34	0.43
1.35Å	0.43	0.33	0.19	0.72	0.68	0.27	0.36
1.54Å	0.34	0.33	0.24	0.65	0.64	0.19	0.29
1.79Å	0.24	0.29	0.26 ¹	0.52	0.55	0.12	0.21
2.28Å	0.11	0.17	0.22	0.28	0.39	0.05	0.12

¹ The maximum value is 0.26 at 1.84Å.

III. OVERLAP AND BONDING POWER FOR VARIOUS TYPES OF ORBITALS

Referring to Fig. 2, taken in connection with Eq. (4), some interesting conclusions can be reached. In agreement with familiar considerations of Pauling, Slater, and others, much greater strength is predicted for $s, p(\sigma)$ hybrid bonds than for either pure s or pure $p\sigma$ bonds; however, contrary to Pauling,² the overlap integral criterion indicates that trigonal and digonal should be somewhat stronger (instead of weaker) than tetrahedral hybrid bonds. Fig. 2 further indicates that $p\sigma$ and hybrid bonds should be long-range bonds, in agreement with Pauling and Slater, but that s and $p\pi$ bonds should be strong only at short range. Fig. 2 (especially if one visualizes how it would look when revised to the improved basis of SCF orbitals--cf. Table I) indicates, contrary to Pauling,² that pure $2p\sigma$ bonds should at best be relatively weak, but that $2s$ and $2p\pi$ bonds should be strong at sufficiently close approach of two atoms.

The foregoing results give a very satisfactory explanation of

some of the major characteristics of single, double, and triple bonds. If two atoms come together to form a single bond, they choose a σ bond, because of its long-range character: either a $2p\sigma$ bond (e.g., $F-F$, $O-O$ in H_2O_2 , or $N-N$ in N_2H_4 ; these are all notably weak), or if possible a $2te\sigma$ bond (e.g., $C-C$ in C_2H_6 ; this is fairly strong in accord with its hybrid character). If two atoms should approach each other to form a double or triple bond, they would be expected first to form a σ bond. This would pull them closely enough together so that a π bond or bonds could begin to take hold, giving a moderately strong double bond (e.g., $O=O$, $N=N$, or $C=C$), or a strong triple bond (e.g., $N\equiv N$ or $C\equiv C$). The great strength of the triple bond in N_2 must be attributed to the fact that, although the $N-N$ σ bond alone (as in N_2H_4) is very weak, and although a single π bond alone does not occur, the cooperative action of one σ and two π bonds pulls the atoms closely enough together so that \underline{S} becomes fairly large for the π bonds, which then become strong.

To make the foregoing discussion more concrete, SCF-orbital \underline{S} values for some representative examples of single and multiple bonds at their normal bond lengths are given in Table II.⁷

TABLE II

SCF-ORBITAL \underline{S} VALUES FOR SOME REPRESENTATIVE BONDS

Bond	R(Å)	Types of Bond and \underline{S} Values
H—H	0.74	$1s$ ($\underline{S} = 0.75$)
Li—Li	2.67	$2s$ ($\underline{S} = 0.59$)
C—C	1.54	$2te$ ($\underline{S} = 0.64$)
C=C	1.35	$2tr$ ($\underline{S} = 0.68$) and $2p\pi_x$ ($\underline{S} = 0.36$)
C≡C	1.20	$2d1$ ($\underline{S} = 0.73$) and $2p\pi$ ($\underline{S} = 0.43$)
F—F	1.44	$2p\sigma$ ($\underline{S} = 0.22$)
C—H	1.10	$2te_C-1s_H$ ($\underline{S} = 0.72$)

The logical next step would be to implement Eq. (4) by determining the empirical constant A for various types of bonds. This can be done, using available data on heats of formation and dissociation, and it is found that A is about 0.7 for $s-s$ bonds (the value is 0.77 for H_2), about 0.95 for other σ bonds (including $C-H$ and $C-C$ σ bonds), and about 1.3 for π bonds. These values (which may be called A_s , A_σ , and A_π respectively) are subject to existing uncertainties about heats of atomization,⁴ particularly for carbon compounds, but it is at any rate clear that A_π is considerably larger than A_σ . This means that the strengths of π bonds are relatively considerably larger than one would conclude from the S values alone. On the other hand, the strengths of $s-s$ bonds are somewhat weaker than their S values would indicate.

Up to this point, it has been tacitly assumed that the heat of atomization can be understood by a consideration of the bonding electrons alone. The form of Eq. (4) embodies this assumption. Actually, it has been known for some time, in fact ever since soon after quantum mechanics began to be applied to valence theory, that the so-called nonbonded repulsions are also of major importance for bond strengths.⁸ There are also nonbonded attractions which are often appreciable, although relatively of minor importance.⁴

Hence to have maximum energetic stability, it is necessary not only that the attractions associated with the bonding electrons shall be as strong as possible, but also that the nonbonded repulsions shall be as weak as possible. Each molecule must then make such choices (σ or π bonds) and adjustments (type and degree of hybridization) as to obtain the best compromise between bonded (plus nonbonded) attractions and nonbonded repulsions.

It may accordingly be wise to acknowledge that the circumstances afforded us by Nature are by no means as simple as we should

like--or as we commonly assume--in the matter of valence theory; and to face the need to take explicit account of the nonbonded as well as the bonding interactions between electrons of atoms in a molecule. An approach to a solution of this problem will be taken up in Section V. To prepare the way, nonbonded repulsions are considered briefly in Section IV.

IV. OVERLAP INTEGRALS AND NONBONDED REPULSIONS

VB theory and MO theory agree^{3,4} in indicating that for every nonbonded pair of electrons of like type, one on each of two neighboring atoms, there is a repulsion energy roughly proportional to S^2 , the square of the overlap integral of the orbitals occupied by the electrons of such a pair. As in the case of bonded attractions, approximate proportionality to I is again reasonable. For the interaction of electrons in closed shells, as in the case of two rare gas atoms, MO theory makes the following expression very plausible:

$$E = \frac{1}{2} \sum_i A_i I_i S_i^2 / (1 - S_i^2) - \frac{1}{2} \sum_k K_k, \quad (6)$$

where the first sum is taken over all interatomic pairs of electrons of like type (that is, both members of a pair σ , or both π), and the A 's (A_σ or A_π) are the same as for bonded pairs. (The K summation in Eq. (6) corresponds to pairs consisting of one σ and one π electron; here theory predicts a nonbonded attraction, appreciable but not large, and independent of S --which in this case is always zero.) Since usually the S 's are small for nonbonded pairs, so that the factor $1/(1 - S_i^2)$ is unimportant, and since, also, experience indicates the need for a little additional empirical flexibility, Eq. (6) may be modified to

$$E = \frac{1}{2} \sum_i A_i S_i^2 I - \frac{1}{2} \sum_k K_k. \quad (6a)$$

One of the simplest examples is the repulsive interaction of two helium atoms at close range. This corresponds to four equal non-bonded electron pair repulsions, all between $1s$ electrons. Eq. (6) then becomes

$$E = 2AIS^2/(1 - S^2) .$$

This expression, with S computed theoretically and $I = 24.58\text{ev}$ taken from experiment, and with A taken as 0.65, is compared in Table III (taken from Ref. 3), over a range of R values, with values of E evaluated by direct theoretical procedures. It is seen that the fit is remarkably good. A similarly good fit over a known range of R values is

TABLE III

VAN DER WAALS REPULSION ENERGY BETWEEN TWO HELIUM ATOMS

R/a_0	2	2.5	3	3.5	4	5
S	0.275	0.161	0.091	0.049	0.026	0.0075
$2AS^2I/(1 - S^2)$ with $A = 0.65$	2.61ev	0.85	0.27	0.077	0.021	0.0018ev
Theoretical	2.38ev	0.81	0.26	0.080	0.025	0.0023ev

obtainable using Eq. (6a) with νA suitably chosen.

A further example of nonbonded repulsions, of a different type, occurs in the interactions between $1s$ H atom electrons in molecules of the type AH_n or A_2H_n . Here no definitely reliable values of actual repulsions between H atoms in such molecules seem to be available, but it is of interest to see how big the overlap integrals are, and from these to estimate the corresponding repulsion energies using the same A value and formula (Eq. (6a)) which is found to fit for the case of two helium atoms. Table IV (from Ref. 3) affords such a survey. It indicates that overlaps of nonbonded H atoms are surprisingly large, and suggests that the corresponding repulsion energy can reach

considerable totals in molecules containing several hydrogen atoms. Further studies of a similar nature indicate that nonbonded repulsion energies between inner shells of one atom and the valence shell of

TABLE IV
OVERLAP OF NONBONDED HYDROGEN ATOMS

Compound	$R_{\text{HH}}, \text{\AA}$	$S_{1s,1s}$	$\frac{1}{2}AS^2I/(1 - S^2)$ with $A = 0.65$
H ₂ O	1.51	0.38	0.75ev
CH ₄ or adjacent H atoms in C ₂ H ₆	1.78	0.28	0.36
C ₂ H ₄ (adjacent H atoms)	1.84	0.26	0.32
C ₆ H ₆	2.46	0.12	0.07

another⁸ may often be very important in the total balance of positive and negative terms making up the net energy of atomization of any molecule.

V. MAGIC FORMULA FOR ATOMIZATION ENERGIES

Following out the line of thought presented in the preceding sections, a "magic formula" has been developed⁴ for the purposes of reproducing or predicting and, especially, of understanding, heats of atomization. While this formula is still rather preliminary as to exact structure and as to the values of the empirical coefficients in it, it is already good enough to reproduce observed energies of atomization for a somewhat varied selection of molecules (CH, N₂, O₂, F₂, CH₄, C₂H₆, C₂H₄, C₂H₂, H₂⁺, He—He repulsion) with an average error of roughly $\pm 10\%$.

The magic formula is as follows:

$$D = \sum_{ij} X_{ij} - \frac{1}{2} \sum_{kl} Y_{kl} - \frac{1}{2} \sum_{mn} K_{mn} - P + RE, \quad (7)$$

\sum_{ij} all electron pair bonds
 \sum_{kl} all nonbonded pairs of electrons not on same atom
 \sum_{mn} all nonbonded pairs of electrons not on same atom

in which $X_{ij} = A_i S_{ij} \bar{I}_{ij} / (1 + S_{ij})$ for the bonded attraction terms,

and $Y_{kl} = 0.7 A_k S_{kl}^2 \bar{I}_{kl}$ for the nonbonded repulsion terms,

with A_i and A_k equal to 1.16 for σ bonds (A_σ) and to 1.53 for π bonds (A_π) to give D in ev (electron-volts). The subscripts $i, j; k, l; m, n$ refer to the atomic orbitals of the electrons concerned, the two members of any pair being on neighboring atoms. The quantities \bar{I}_{ij} or \bar{I}_{kl} refer to mean ionization energies, an average being taken for the two orbitals involved.⁹ The nonbonded attraction terms K_{mn} , which involve σ - π pairs, are not functions of overlap integrals, but can be computed theoretically.¹⁰ The promotion energy correction P , which is a sum of individual contributions from the various atoms, is often of considerable importance. Such a correction necessarily occurs whenever an atom has to be promoted from its ground state to a state of higher energy (valence state) before it can function as required in the particular compound.⁹ For carbon in its tetravalent compounds, the promotion energy is always large. Finally, RE in Eqs. (7) denotes resonance energy of one kind or another,⁹ including corrections for the extra stability which (as Pauling pointed out) occurs for bonds between atoms differing in electronegativity. However, Eq. (7) is not intended to apply to molecules containing truly ionic bonds.

The meaning and use of Eq. (7) can best be made clear in terms of an example. For this purpose,⁴ the CH radical is convenient. If s,p hybridization is ignored, the electron configuration according to VB theory would be:

$$(1s_C)^2 (2s_C)^2 (2p\sigma_C \cdot 1s_H) (2p\pi_C) ,$$

there being a single C—H bond formed by the carbon $2p\sigma$ orbital with the $1s$ hydrogen orbital; the bond is indicated by a dot in the above configuration symbolism. When hybridization is admitted, the electron configuration becomes

$$(1s_C)^2 (2h'_C)^2 (2h_C \cdot 1s_H) (2p\pi_C) , \quad (8)$$

where $2h$ and $2h'$ are two mutually orthogonal $2s$ - $2p\sigma$ hybrid orbitals of the forms

$$2h = \alpha 2s + (1 - \alpha^2)^{\frac{1}{2}} 2p\sigma ; \quad 2h' = (1 - \alpha^2)^{\frac{1}{2}} 2s - \alpha 2p\sigma . \quad (9)$$

The hybrid $2h$ is a positive hybrid,⁶ strong in the direction of the hydrogen atom, while $2h'$ is a negative hybrid,⁶ weak in that direction and strong in the opposite direction. The special case $\alpha = \frac{1}{2}$ would correspond to a tetrahedral orbital, but it is not necessary here to assume any particular value of α in advance. On the contrary, as will be seen, the magic formula can be used to determine what value of α will give the strongest bonding.

Corresponding to Eq. (8), Eqs. (7) take the form⁷

For greater ease of writing, the subscripts 1, 1, and so on, of Eqs. (7) are here replaced by expressions in parentheses.

$$D = X(2h_C, 1s_H) - (2/2)Y(1s_C, 1s_H) - (2/2)Y(2h'_C, 1s_H) + \frac{1}{2}K(2p\pi_C, 1s_H) - P,$$

$$\text{with } X(2h_C, 1s_H) = A_{\sigma} \bar{I}_{CH} S(2h_C, 1s_H) / [1 + S(2h_C, 1s_H)] ,$$

$$Y(1s_C, 1s_H) = 0.7 A_{\sigma} \bar{I}(1s_C, 1s_H) S^2(1s_C, 1s_H) ,$$

$$\text{and } Y(2h'_C, 1s_H) = 0.7 A_{\sigma} \bar{I}_{CH} S^2(2h'_C, 1s_H) .$$

(10)

The value of A_C is 1.16; that of $\bar{I}(1s_C, 1s_H)$ is 151ev, while $\bar{I}_{CH} = 14.24\text{ev}$.⁴ In Eqs. (10), $S(2h_C, 1s_H)$ and $S(2h'_C, 1s_H)$, as well as P , depend⁴ on the hybridization coefficient α . One can thus use Eq. (10) to compute D for any value of α , and if the values so computed are plotted against the "degree of hybridization" α^2 , it is found that the computed D has a maximum value at $\alpha^2 = 0.155$. (This degree of hybridization can be shown⁴ to be equivalent to 15.5% promotion of the carbon atom from its normal s^2p^2 configuration toward sp^3 .) It is reasonable⁴ to believe that the value thus obtained is close to the true value.¹¹ One notes that the degree of hybridization in $2h_C$ so determined is considerably less than for a tetrahedral hybrid.

The following Table V, taken from Ref. 4, shows in a very instructive way how hybridization affects the various terms, and so the value of D , given by Eqs. (10). Particularly notable is the fact that

TABLE V
STRUCTURE OF D FOR CH BY MAGIC FORMULA⁴

	$\alpha = 0$ in Eq. (9)	$\alpha = (0.155)^{\frac{1}{2}}$ in Eq. (9)
$S(2h_C, 1s_H)$	0.509	0.686
$S(1s_C, 1s_H)$	0.071	0.071
$S(2h'_C, 1s_H)$	0.553	0.308
$X(2h_C, 1s_H)$	5.57ev	6.73ev
$-Y(1s_C, 1s_H)$	-0.62	-0.62
$-Y(2h'_C, 1s_H)$	-3.54	-1.09
$\frac{1}{2}K(2p\pi_C, 1s_H)$	0.40	0.40
$-P$	-0.49	-1.95
D calculated	1.32ev	3.47
		(Observed $D = 3.47\text{ev}$)

hybridization has an important effect not merely in strengthening the bonding between the hydrogen electron and the $2h_C$ bonding orbital, but also in cutting down the otherwise rather large nonbonded repulsion between the hydrogen electron and the $(2h'_C)^2$ lone pair of carbon electrons. Other notable points are the considerable size of the nonbonded repulsion between the H atom electron and the inner shell ($1s$) carbon electrons, and of the nonbonded attraction between the H atom electron and the $2p_\pi$ carbon electron. All the effects noted here in the example of CH recur with comparable importance for other molecules.

Another instructive example is the nitrogen molecule (see Ref. 4 for details). Here for no hybridization (pure s^2p^3 trivalence) the magic formula gives $\underline{D} = -0.04\text{ev}$, while for optimum hybridization, which turns out to correspond to 21 percent promotion from s^2p^3 toward sp^4 trivalence, the computed \underline{D} is 8.32ev, near the observed value. Notable also is the large magnitude of the nonbonded repulsions exerted by the inner ($1s$) shells (-4.3ev altogether, almost half the net \underline{D}). Still more notable is the fact that, according to the magic formula, it is essentially the π electrons alone which give the triple bond in N_2 its great strength. Their calculated contribution to \underline{D} is 14.97ev; the sum of all other contributions, for $\alpha^2 = 0.21$, is -6.65ev. The promotion energy \underline{P} is 8.84ev.

Because of the preliminary character of the magic formula, no great reliance should be placed on the exact quantitative figures given above, but there seems to be little doubt that the corresponding major qualitative conclusions, at least, are correct.

Even though the magic formula is still in a preliminary edition, in need of further development and testing as to its quantitative possibilities, it should probably already have a number of interesting applications to the rough estimation of bond energies, in addition to the

insight it gives into the way in which actual net bond energies are built out of a number of positive and negative contributions. For example, it may be useful in estimating how bond energy depends on bond angles, in estimating the energies of free radicals and of molecules in excited and ionized states (in some cases Eqs. (7) then need additional terms⁴), and in estimating steric repulsions; and it should be capable of extension to metals. Finally, it gives definite and probably rather reliable conclusions as to degrees of isovalent hybridization, that is, of hybridization of the kind illustrated in CH and N₂ above, where σ bonds of increased strength are formed by hybridization without increase in the number of bonds. It is of interest that the degrees of isovalent hybridization indicated by the magic formula are in good accord⁴ with rough values indicated by several other lines of evidence for molecules such as HCl, H₂O, NH₃, N₂, and O₂.

REFERENCES

- ¹ This work was assisted by the ONR under Task Order IX of Contract N6ori-20 with The University of Chicago.
- ² Pauling (see Section 13 of his well-known book) uses a different index of bond strength. This measures the extent to which any bond orbital sticks out toward another atom, and for 2-quantum orbitals has the values 2 for 2te, $\sqrt{3}$ for 2p σ , and 1 for 2s. It is not defined for π bonds, and is open to other objections (see Ref. 3).
- ³ R. S. Mulliken, J. Am. Chem. Soc., **72**, 4493 (1950).
- ⁴ R. S. Mulliken, J. Phys. Chem., **56**, 295 (1952).
- ⁵ Cf. Mulliken, Rieke, Orloff, and Orloff, J. Chem. Phys., **17**, 1248 (1949), and Refs. 3 and 6.

- ⁶ R. S. Mulliken, J. Chem. Phys., 19, 900 (1951). See Tables VB ($\alpha = 0.5$) and VI for comparison of Slater and SCF overlap integrals. The carbon-carbon SCF S tables can also be adapted to give fairly accurate SCF S values for N—N, O—O, and F—F overlaps (see footnote 42 of Ref. 4).
- ⁷ For a survey of corresponding bond energies, see Ref. 4; in particular Table VII for an instructive (though over-simplified) presentation of some of these.
- ⁸ See K. S. Pitzer, J. Am. Chem. Soc., 70, 2140 (1948) for an interesting recent discussion. (Cf. also Ref. 3.)
- ⁹ See Section IV of Ref. 4 for a more complete discussion.
- ¹⁰ The necessary formulas have been given by K. Rüdénberg, J. Chem. Phys., 19, 1459 (1951). See Ref. 4, in particular footnote 31, for further explanation.
- ¹¹ The value 1.16 of \underline{A}_0 used here was, in fact, determined⁴ by plotting \underline{D} as given by Eq. (10) for CH as a function of α for various trial values of \underline{A}_0 , until a value was found such that \underline{D} at the maximum of the corresponding $\underline{D}(\alpha)$ graph was equal to the observed \underline{D} for CH.

CAPTIONS FOR FIGURES

Figure 1. Forms of some 2-quantum atomic orbitals (schematic: see text) drawn to show how like orbitals of two atoms overlap when the atoms are pushed together (imagine the interatomic distance R to be gradually decreased).

Figure 2. Overlap integral S based on Slater orbitals for 2-quantum homopolar bonds. The symbols te, tr, di, refer respectively to tetrahedral, trigonal, and digonal hybrid bonds ($\alpha = \frac{1}{2}$, $(1/3)^{\frac{1}{2}}$, and $(\frac{1}{2})^{\frac{1}{2}}$ in Eqs. (5)). The lower scale is for the interatomic distance R in Å.U. for carbon-carbon bonds. With the use of the upper p scale, the figure is applicable to any second-row homopolar bond; p means $ZR/2a_0$, where Z is the Slater Z value (cf. Ref. 5). The circles superimposed on some of the curves are at $R_{CC} = 1.54\text{Å}$ (C—C bond, small full circle), $R_{CC} = 1.35\text{Å}$ (C=C bond, open circles), and at $R_{CC} = 1.20\text{Å}$ (C≡C bond, double open circles). For SCF orbitals, the $2p\pi$ curve would be raised and the $2p\sigma$ curve lowered considerably, and the others changed to lesser extents (cf. Table I).



$$\chi_{2sa} = F_{2s}(r_a)$$

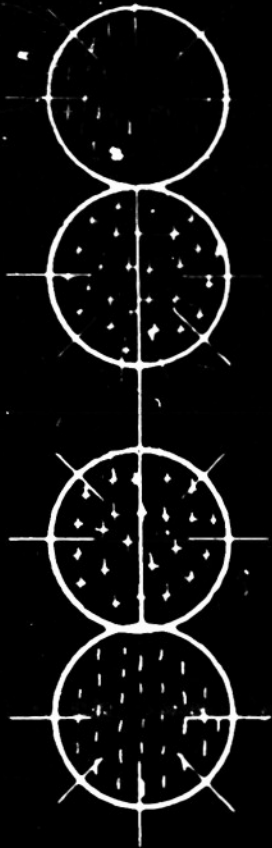
$$\chi_{2pa}$$



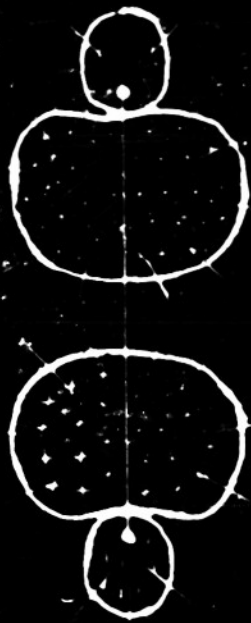
$$\chi_{2pb}$$



R



$$\chi_{2p\sigma_a} = F_{2p}(r_a) \sqrt{3} \cos \theta_a$$



$$\chi_{2te} = \sqrt{1/2} (\chi_{2s} + \sqrt{3} \chi_{2p\sigma})$$

$$\text{Overlap Integral, } S(R) = \int^{\infty} \chi_a^* \chi_b d\tau$$

